Synthesis and Optical Properties of Poly(1,4-(2-(5-carboxypentyloxy)-5-methoxyphenylene)vinylene)

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Conducting polymers with highly extended π-electron systems in their main chains have attracted much interest from both fundamental and practical viewpoints. In various conducting polymers, poly(*p*-phenylene vinylene) (PPV) and its derivatives are the most attractive materials for light-emitting diodes and lasers [1-3], because of their high solubility in common organic solvents and the high luminescence quantum efficiency.

Recently, we utilized poly(3-thiophene acetic acid), the side chain of which includes a carboxylic substituent in a monomer unit, for fabrication of the multilayered polymer system by the self-assembly technique [4,5]. Similar substituents could be introduced into the PPV derivatives, which must have high luminescent properties due to the PPV backbone.

In this paper, synthesis and optical properties of poly(1,4-(2-(5-carboxypentyloxy)-5-methoxyphenylene)vinylene) (CPMOPPV) are reported, and yellow EL are also demonstrated.

CPMOPPV was synthesized by modifying the procedures used for the preparation of ROPPV as follows [2,3,6]. 6-(4-Methoxyphenyloxy)-hexanoic acid ethyl ester was prepared by treating hydroquinone monomethyl ether with 1-bromohexanoic acid ethyl ester and sodium methoxide. 6-(4-Methoxyphenyloxy)-hexanoic acid ethyl ester was then chloromethylated by treating with an excess amount of formaldehyde and hydrochloric acid in dioxane, to afford 6-(2,5-bis(chloromethyl)-4-methoxyphenyloxy)-hexanoic acid ethyl ester. The product was purified by recrystallization from n-hexane.

CPMOPPV was prepared by dehydrochlorination polymerization of 6-(2,5-bis(chloromethyl)-4-methoxyphenyloxy)-hexanoic acid ethyl ester with potassium tert-butoxide. Namely, 2-methyl-2-propanol solution of potassium tert-butoxide was added dropwise to monomer solution with *p*-xylene and 2-methyl-2-propanol (1:1) at room temperature in an inert atmosphere, and the mixture was refluxed for 24 h. The orange precipitate formed was recovered by filtration, and resolved to be an aqueous solution. Hydrochloric acid was added into the aqueous solution to obtain the orange precipitate of CPMOPPV. The molecular structure of CPMOPPV is shown in the inset of Fig. 1. The polymer is soluble in common organic solvents such as acetone, ethanol and tetrahydrofuran (THF). The sodium salt of CPMOPPV, which could be obtained by adding sodium hydroxide (NaOH), is soluble even in water.

The obtained polymer, CPMOPPV, was an orange lump and an orange solution was easily prepared by dissolving the lump in common organic solvents such as acetone, ethanol and THF at room temperature. Elemental analysis of the composition of the polymer (C: 69.1%; H: 7.5%) coincided with the theoretical values (C: 68.7%; H: 6.9%).

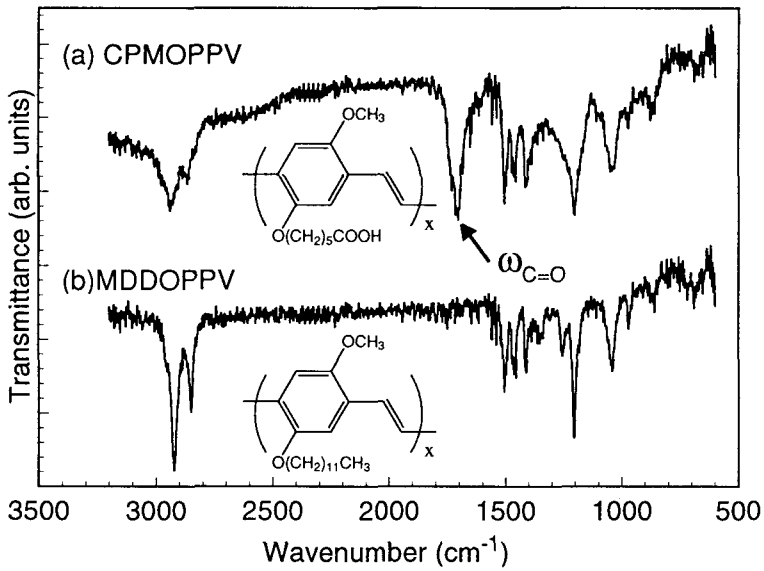

Fig. 1. Fourier transform infrared spectra of CPMOPPV (a) and MDDOPPV (b). Inset shows the molecular structures of CPMOPPV and MDDOPPV.

Figure 1 shows the infrared spectra of CPMOPPV (a) and poly(2-methoxy-5-dodecyloxy-p-phenylenevinylene) (MDDOPPV) (b). These spectra coincided with each other exactly except for the strong absorption peak at around 1700 cm^{-1} for CPMOPPV which indicates the absorption of the stretching mode on the C=O double bonds. The peak indicates that CPMOPPV retained the substituent with carboxy acid as a side chain throughout the polymerization process.

Figure 2 shows the absorption and phtoluminescence (PL) spectra of CPMOPPV. From an analysis of the absorption spectral edge, the band-gap energy of CPMOPPV was evaluated as 2.4 eV. The top of the valence band, that is, the HOMO, was determined from the observed threshold potential of the electrochemical oxidation in the typical cyclic voltammogram of CPMOPPV in LiBF4/PC to be lower than the work function of silver by 0.3 eV.

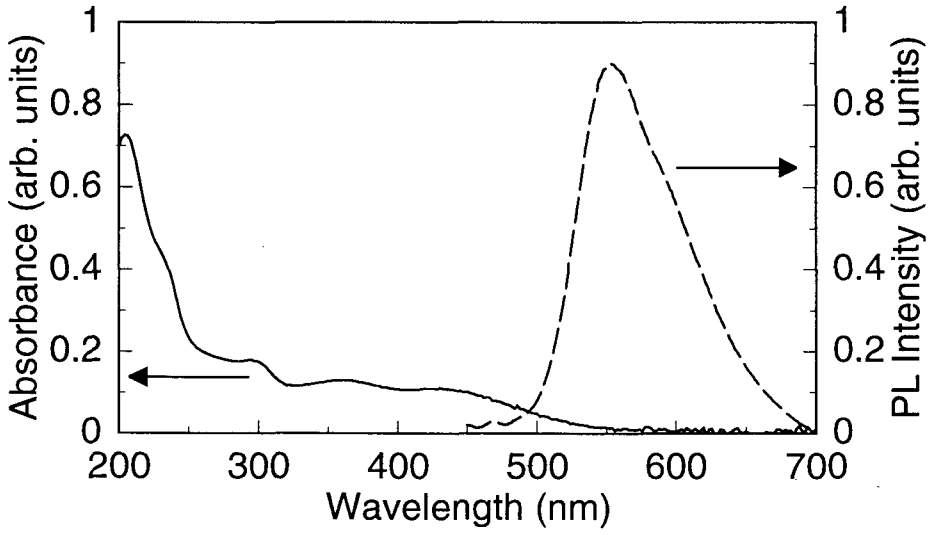

Fig. 2. Absorption and PL spectra of CPMOPPV thin film.

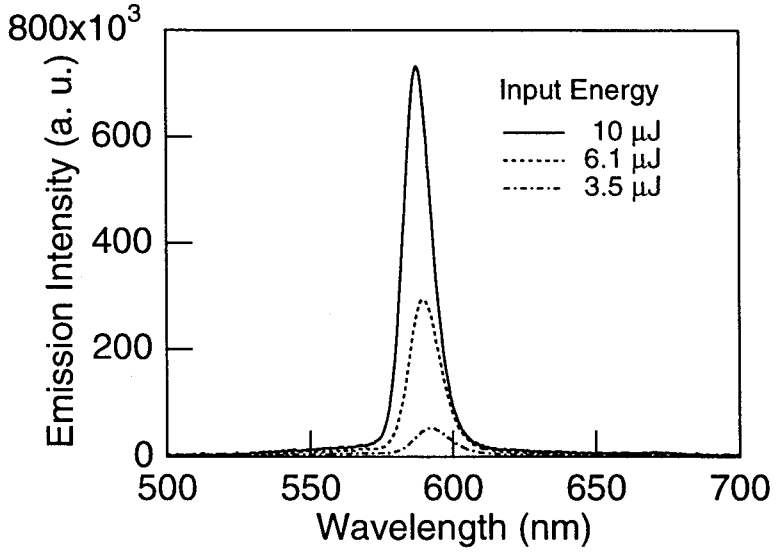

Fig. 3. Optical emission spectra at different excitation pulse energies in CPMOPPV thin film.

PL quantum efficiency of the polymer film was evaluated to be about 7% at least, when 457.9 nm light of an Ar^+ laser was adopted as an excitation source. For the PL measurements at high excitation intensities, we used a laser beam with 600 ps pulses with the energy per pulse ranging from 1 to 110 μJ, provided by a nitrogen laser, the wavelength of which was 337.1 nm. When the excitation intensity was increased, the emission spectra of CPMOPPV film changed as shown in Fig. 3. It is seen that the broad PL spectrum obtained at low excitation intensities changes at high excitation intensities to a much narrower and stronger emission band peaked at 588 nm with the spectral width of 10 nm. The emission spectral narrowing is accompanied by a nonlinear amplification. The sharp peak starts to be observed at the input energy of 2 μJ/pulse and the intensity of the peak at 588 nm changes its dependence on excitation intensity to superlinear.

In an EL diode utilizing CPMOPPV as an emission layer, that is, with a structure of ITO/CPMOPPV/Al, a

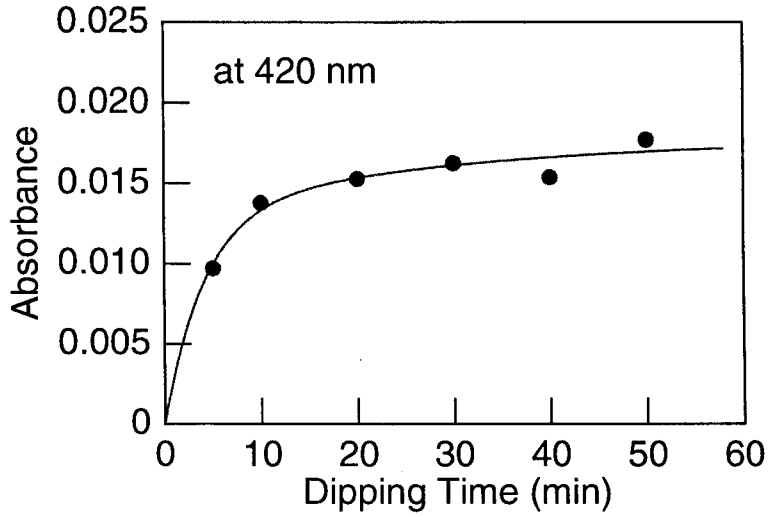

Fig. 4. Time-dependent absorption intensity at 420 nm for the CPMOPPV film adsorbed onto the positively charged surface.

strong yellow electroluminescence was observed. The EL diodes exhibit typical rectifying characteristics. The emission intensity starts to increase at around 15 V, and continues increasing monotonically with increasing injection current. By applying a positive bias voltage to the CPMOPPV EL diodes, a bright yellow emission was obtained at room temperature in vacuum.

Since CPMOPPV has a carboxylic substituent in each monomer unit, it could be ionized in aqueous solution. Namely, CPMOPPV should have negative ions in the polymer side-chains, which implies that CPMOPPV could be one of the candidate polyanions for the multilayer structure by the self-assembly technique. Coulombic force between positively and negatively charged conducting polymers used in the self-assembly method enables the formation of the alternating heterostructure. [4,5]. CPMOPPV should, therefore, be adsorbed onto the positively charged substrate because of the negatively charged side-chains of CPMOPPV.

Figures 4 shows the time-dependent absorption intensity at 420 nm for a CPMOPPV film adsorbed onto a positively charged quartz substrate. CPMOPPV was completely adsorbed onto the positively charged substrate immersed in methanol solution of CPMOPPV for about 20 min. and the absorbance at 420 nm was saturated thereafter. CPMOPPV, therefore, is expected to be an appropriate polyanion in the self-assembly technique and to maintain the high luminescent properties even in a self-assembled multilayer structure.

In conclusions, we succeeded in the synthesis of novel carboxy-substituted PPV, CPMOPPV. The obtained polymer was highly soluble in organic solvents, such as acetone and ethanol, and the sodium salt of CPMOPPV was even soluble in water. Optical properties of CPMOPPV, such as optical absorption and PL were investigated, and yellow EL devices could be fabricated. We suggested that CPMOPPV was a suitable candidate polyanion for fabrication of multilayer structure by the self-assembly technique.

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